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(54) PHOSPHATE COATING AND COATING COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the coating of surfaces using a coating composition comprising a complex phosphate of aluminium.

According to the present invention there is provided a method of coating a surface with aluminium phosphate or a deposit containing aluminium phosphate which comprises the steps of applying to the said surface a composition comprising a solution containing a halogen-containing complex phosphate of aluminium containing at least one chemically-bound molecule of a hydroxy compound R—OH wherein R is a hydrogen atom or an organic group, and removing the solvent of said composition.

The complex phosphates containing chemically-bound molecules of an organic hydroxy compound are described below and in our co-pending UK patent application 29862/69 (Serial No. 1322722), from which the present application is a divisional application. Complex phosphates containing chemically-bound molecules of water are described below, and solid complexes are the subject of our co-pending UK patent application 1737/73 (Serial No. 1322724) which, like the present application, is a divisional from application 29862/69.

The term "phosphate" includes acid phosphates but not phosphate esters.

Where R is an organic group, it is preferred

that it be an aliphatic hydrocarbon group or a substituted aliphatic hydrocarbon group, for example wherein the substituent is one or more of the following: phenyl, hydroxyl, carboxyl or alkoxy. Unsubstituted aliphatic alcohols are especially preferred as the hydroxy compound since the complex phosphates containing them are easily separated solids obtainable in high yield. We have found that aliphatic alcohols containing one to ten carbon atoms are especially suitable, and owing to their ready availability we prefer to use aliphatic alcohols containing from one to four carbon atoms, for example, methanol, ethyl alcohol, n-propyl alcohol or isopropyl alcohol. In preferred embodiments of the invention, ethyl alcohol is used, as the complex phosphates containing it are especially readily formed as solids in high yield.

The halogen in the halogen-containing complex phosphate of aluminium is preferably chlorine, but the compounds may contain other halogens, for example bromine or iodine.

The ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus in the complex phosphates of aluminium may vary over a wide range, for example from 1:2 to 2:1, but is preferably substantially 1:1 as the complex phosphates having this ratio decompose at low temperatures directly to form aluminium orthophosphate having greater chemical stability and refractoriness than aluminium phosphate formed from complex phosphates with other ratios. The ratio of the number of gram atoms of aluminium to the number of gram atoms of halogen in the complex phosphates is preferably substantially 1:1.

The complex phosphates may be monomeric or polymeric.

[Pri]

The structure of the complex phosphates is not fully understood and some of the chemically-bound hydroxy compounds may be bound as groups —OR rather than as complete molecules.

The monomeric forms, or the repeating units of the polymeric forms of the complex phosphates, may contain, for example, from one to five molecules of the hydroxy compound. Most frequently the number of molecules of the hydroxy compound is 4. In some cases the complex phosphates may contain molecules of different hydroxy compounds, for example they may contain both chemically-bound water and a chemically-bound organic hydroxy compound, the total number of such molecules being, for example, from 2 to 5.

An example of a complex phosphate which may be used is the complex phosphate containing ethyl alcohol and having the empirical formula $\text{AlPClH}_{11}\text{C}_2\text{O}_5$. The infra-red and X-ray characteristics of the compound are as hereinafter described. This compound is designated aluminium chlorophosphate ethanolate, for convenience referred to herein as ACPE, but it is to be understood that this designation in no way implies any particular molecular structure for the compound.

An example of a complex phosphate containing chemically-bound water is the complex phosphate containing chemically-bound water having the empirical formula $\text{AlPClH}_{11}\text{O}_5$. The infra-red and X-ray characteristics of the compound are as hereinafter described. This compound is designated aluminium chloro-phosphate hydrate, for convenience referred to as ACPH, but it is to be understood that this designation in no way implies any particular molecular structure for the compound.

A further example of a complex phosphate is that containing bromine and ethyl alcohol having an empirical formula $\text{AlPBrH}_{11}\text{C}_2\text{O}_5$.

The infra-red and X-ray characteristics of the compound are as hereinafter described. This compound is designated aluminium bromo-phosphate ethanolate, for convenience referred to as ABPH, but it is to be understood that this designation in no way implies any particular molecular structure for the compound.

The complex phosphates, containing at least one chemically-bound molecule of an organic hydroxy compound, are generally soluble in water and organic solvents, especially polar organic solvents. Complex phosphates containing chemically-bound water molecules are soluble in water. Their solubility in solvent mixtures increases as the proportion of polar solvent in the solvent mixture increases. Solvents comprising water and a water-miscible organic solvent are especially convenient for dissolving the complex phosphates. Solubility generally increases as the pH of the solution is decreased, and it is preferable to establish a pH of less

than 2.5 in water solutions to maintain maximum solubility. The complex phosphates generally give viscous solutions in water.

Thus there may be formed a homogeneous composition comprising a phosphate of aluminium and an organic solvent derived from a complex phosphate of the invention and an organic solvent. The composition may contain water or it may be substantially anhydrous. The organic solvent is preferably a liquid at ordinary temperatures. The organic solvent is preferably a polar solvent, especially an oxygen-containing polar solvent. Especially useful are aliphatic alcohols containing up to 10 carbon atoms, esters, polyhydric alcohols, and glycol esters. Most preferred are aliphatic alcohols containing from 1 to 5 carbon atoms, for example methanol or ethanol. The solvent may be a mixture of solvents. The ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus in the composition may vary over a wide range, for example from 1:2 to 1.5:1, but is preferably substantially 1:1, as aluminium phosphate formed by decomposition of a composition having this ratio is especially stable.

Thus, according to a further aspect of the invention there is provided a coating composition comprising a solution containing a halogen-containing complex phosphate of aluminium containing at least one chemically-bound molecule of a hydroxy compound R—OH which is an aliphatic alcohol containing 1 to 4 carbon atoms.

The complex phosphates or mixtures containing the said complex phosphates, for example their solutions, may be prepared, for example, by reacting aluminium or an aluminium compound, preferably a halide with a hydroxy compound R—OH and phosphoric acid. If desired, the phosphoric acid may be formed in situ by using a compound capable of forming phosphoric acid under the reaction conditions, for example The aluminium halide may be a simple halide or an oxyhalide or an aluminium alkoxy halide, for example aluminium ethoxy chloride. Other suitable aluminium compounds include aluminium alkoxides, for example aluminium ethoxide. When aluminium or an aluminium compound other than a halide is used, the presence of a halogen acid is necessary. Mixtures of hydroxy compounds may be used, phosphorus pentoxide, phosphorus oxyhalides and phosphorus halides may be used in the presence of water. An aqueous solution of phosphoric acid may be used, conveniently an 88% solution in water, although it is preferred to ensure that no more than about 5% by weight of water based on the total weight of reaction mixture is present when a complex phosphate containing an organic hydroxy compound is prepared, thereby avoiding a loss of yield.

The order in which the reactants are added to one another is not critical; we prefer to add

the aluminium compound to the hydroxy compound and then to react the phosphoric acid with the resultant mixture. It may be convenient to dissolve the aluminium compound in a suitable solvent, which may be either the hydroxy compound or an inert solvent, before reacting it further. This is especially convenient when the hydroxy compound is a solid at the temperature at which the reaction is carried out or when it is a poor solvent for the aluminium compound.

The highest yields of product are obtained when the molar ratio of aluminium to phosphorus in the reaction is substantially 1:1.

The reaction may be carried out over a wide range of temperature, but generally we prefer to use a temperature below 60°C and preferably from 0°C to 50°C, to obtain optimum yields.

It is preferred, for example when it is desired to preserve anhydrous conditions, to carry out the reaction in an atmosphere of a dry inert gas, for example, nitrogen.

Complex phosphates containing chemically-bound water molecules or a mixture containing the said complex phosphate may also be prepared by the hydrolysis of another complex phosphate which contains a chemically-bound organic hydroxy compound, or by carrying out the reactions hereinbefore described in the presence of water. By this means it is possible to replace, wholly or partially, the organic hydroxy compound with water molecules. It is especially convenient to use as starting material the complex phosphate having the empirical formula $\text{AlPClH}_{25}\text{C}_8\text{O}_8$. The partially hydrolysed product may be a single substance containing both chemically-bound water and the organic hydroxy compound or it may be a mixture of, for example, wholly hydrolysed and unhydrolysed molecules of the original complex phosphate. Polymerisation of the hydrolysis product may accompany hydrolysis so that higher molecular weight products are formed. Hydrolysis may be effected by any convenient means, but for many of the complex phosphates it is sufficient to add water at room temperature or to keep the compounds in contact with moist air for a sufficient time. Conveniently this is done by fluidising the compound in a stream of humidified air, preferably at a temperature below 80°C.

The complex phosphate may be used without isolation from the mixture from which it is formed or after removal of part of the reaction products.

Thus the crude reaction product mixture of the process employed may be used directly for at least some of the applications hereinafter described, for example, the coating of metals. Alternatively, a solid comprising the complex phosphate may be separated from the reaction mixture and used as such or optionally further purified before use. Separation of the product may be effected by any convenient means, for

example by precipitation by cooling, evaporation of volatile constituents or addition of a further component, followed by filtration or by chromatography. In some cases spontaneous precipitation of the product from the reaction mixture occurs, and separation is effected simply by filtration. The product may be washed, for example with ethanol. The mother liquor left after separation of the product may be discarded or recycled for further use, preferably after purification from unwanted side-products of the reaction.

The complex phosphates used in the invention decompose on heating to give aluminium phosphate in amorphous or various crystalline forms. The temperature at which aluminium phosphate forms depends upon the particular complex phosphate heated, but is normally from 80°C to 500°C, and is often below 100°C. It is convenient to heat the complex phosphate to a temperature from 100°C to 150°C to form aluminium phosphate. Surprisingly, crystal forms of aluminium phosphate can be obtained at low temperatures which are normally obtained only by heating aluminium phosphate to temperatures in excess of 800°C. The aluminium phosphate may be further heated, for example to change its crystalline form. When the gram atom ratio of aluminium to phosphorus in the complex phosphate is 1:1 the aluminium phosphate produced has the same ratio of aluminium to phosphorus and is consequently particularly chemically stable. The properties of aluminium phosphate are such as to confer on the coatings produced by the process of the invention desirable properties such as strength, refractoriness or chemical inertness.

Solutions of complex phosphates used in the invention may conveniently comprise additional components, for example material which will aid the further processing of the solutions or desirably affect the products formed from the solutions. Thus organic materials, especially polymers, may be dissolved in the complex phosphate solution, especially in cases where the solvent is an organic solvent. Additional components, for example pigments, colorants or fillers, may likewise be dispersed in the solutions of the complex phosphates. It is especially preferred that the solution of complex phosphate comprises a material or materials which control the physical nature of the solid phase of aluminium phosphate which is produced from the solution, for example by heating. When the solvent comprises water it is preferred to use a crystallisation stabiliser, for example finely divided silica or alumina, or a nucleation activator or catalyst, for example dibutyl peroxide, or calcium, magnesium or sodium chloride. When the solution of the complex phosphate is non-aqueous, for example when the solvent is ethanol, it is preferred to use a boric acid ester or ether or a silicic acid ester or ether, for example methyl borate, tri-

methoxy boroxine or ethyl silicate to suppress the crystallisation of aluminium phosphate.

5 Solutions of the complex phosphate in water or organic solvents may be used to produce coatings of aluminium phosphate for a number of surfaces, by removal of solvent and preferably heating of the deposited coating. The duration of heating is preferably at least 10 minutes. The form of aluminium phosphate produced will depend, amongst other things, upon the temperature to which the coating is heated, although a temperature of at least 80°C is normally sufficient to form a coat of aluminium phosphate. Preferably the coating is heated to a temperature from 100°C to 200°C. The coating may be further heated to polymerise the deposit or to change the crystal form of aluminium phosphate. Especially for coatings produced from a solution of complex phosphate in organic solvents, the aluminium phosphate may be prevented from crystallising by the use of boric acid esters or ethers or silicic acid esters or ethers as hereinbefore described. Organic materials, preferably polymers, may be dissolved in the solutions from which the coatings are produced to give coatings comprising an organic material and aluminium phosphate. It is advantageous to add a suitable wetting agent to the coating solution to assist uniform coating. Other components, for example pigments, may be incorporated in the coating by including them in the coating solution.

35 The invention therefore provides a method for coating any substrate, for example glass, carbon, metals, ceramics or organic polymers, with a film of aluminium phosphate. It is preferable for the substrate to be capable of withstanding a temperature of at least 80°C; for substrates which will not withstand this temperature, coating is preferably heated by a method which does not heat the surface on which it is deposited, for example, by microwave heating. The coating of aluminium phosphate is useful in a number of ways, for example protection of the substrate against corrosion or abrasion. Any desired shape of substrate surface may be coated, for example fibres, films, powdered and manufactured objects. ACPE, especially when dissolved in a polar solvent, is especially useful for providing a coating solution. Surfaces coated with aluminium phosphate may be coated with a further component, for example with a metal such as aluminium.

55 Solutions of the complex phosphates are especially useful for coating glass since bonding between the glass surface and aluminium phosphate is very good. It is especially advantageous if the coating is applied immediately the glass is formed from its melt. The sizing of glass fibre by means of solutions of the complex phosphates is particularly useful. Thus, according to a further aspect of the invention there is provided glass fibre coated with alu-

minium phosphate or a deposit containing aluminium phosphate. The solution is preferably applied to the glass fibre immediately after the fibre is extruded. After application, the solution is dried either in a vacuum or by heating or by a combination of both. Heating of the coating to form aluminium phosphate, which is referred to herein as curing, may be combined with the drying stage. For example, if ethyl cellulose is used as solvent for the complex phosphate, curing and drying may be carried out at the boiling point of the solvent, which is 135°C. When, however, the solvent is removed at a temperature less than about 80°C, further heating of the coating at a temperature of at least 80°C is necessary to effect curing. Solutions of the complex phosphates in organic solvents may comprise materials such as organosilanes or organic resins such as hydroxypropyl cellulose, epoxy resin or low molecular weight urea-formaldehyde resin to reduce the permeability of the coat; the resin should be capable of withstanding a temperature of at least 100°C and could, with advantage, be capable of crosslinking at this temperature. Crystallisation-control additives may be incorporated in the coating solutions, for example methyl borate or ethyl silicate.

Other coatings may be applied to the coated glass, for example a resin. Glass coated with aluminium phosphate may be treated with an agent, for example an organo-silicon compound, to aid the incorporation of glass fibre in resin matrices.

Glass thus coated is considerably stronger than uncoated glass, and is resistant to abrasion. It is also more resistant to chemical attack and can thus be used in contact with materials which normally damage glass, for example cement.

Forms of glass other than glass fibre may be coated as hereinbefore described, for example sheet glass and glass articles generally. Glass coated with aluminium phosphate may be further coated with a material which adheres to aluminium phosphate, for example aluminium. Glass fibre thereby coated with aluminium can readily form useful composite materials of glass fibre and aluminium, for example by compression, preferably at an elevated temperature, of a mass of coated glass fibre.

The use of complex phosphates to provide a coating of aluminium phosphate for carbon fibre is especially advantageous. Thus, according to a further aspect of the present invention there is provided a carbon fibre coated with aluminium phosphate or a deposit containing aluminium phosphate. The carbon fibre may, for example, be immersed in solutions of the complex phosphates in water or organic solvents, for example polar solvents such as ethanol, excess solution drained off and the fibre dried, conveniently by heating the fibre in air at temperatures from 90°C to 250°C. Optionally, the fibre may be degreased in, for ex-

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ample, trichloroethylene before application of the solution. The coating may be cured by heating, preferably in an inert gas, for example nitrogen, at a temperature greater than 100°C, conveniently at from 100°C to 500°C, although if drying has taken place at above about 100°C, curing is not always necessary. A coating of aluminium phosphate thus provided on carbon fibre markedly increases the resistance of the fibre to oxidation and protects the fibre surface from interaction between it and other materials with which it comes into contact. Protection may therefore be afforded to the carbon fibre when it is incorporated in materials such as molten metals, for example aluminium, to provide reinforcement for the solid metal. Coating of carbon fibre with aluminium phosphate enables the fibre to be coated further with a film of aluminium metal or glass. Composite materials may be produced by compressing "bundles" of fibres so coated, at high temperature. The coating also produces stronger bonding between the carbon fibre and a siliceous material in which it is incorporated. The complex phosphates may be applied as a glaze or decorative coating to clay-ware or ceramic objects and are useful in general for coating any body which forms a strong bond with aluminium phosphate, although it will be understood that their use is not restricted to examples where such strong bonds are possible. Ceramic fibres may usefully be coated, for example asbestos, silicon carbide fibre and boron fibre.

The process of the invention is useful for

coating metals, for example aluminium and steel. Metal wires may conveniently be protected by the coatings. Corrosion inhibitors, for example glyceryl monolaurate, may be included in the coating solution.

Polymeric organic materials, for example synthetic fibres of nylon or a polyester may conveniently be coated with aluminium phosphate or a mixture comprising aluminium phosphate and an organic material. Drying and curing of the coating may be carried out by any convenient method of heating if the polymer will withstand a temperature of at least 80°C.

The invention is illustrated but not limited by the following Examples.

Example 1

40 gram of anhydrous aluminium chloride was added to 300 ml of laboratory grade ethyl alcohol. The resultant solution was cooled to 0°C and 18.6 ml of 88% orthophosphoric acid was added to it in a drop-wise manner and the reaction mixture stirred. The reaction was carried out in an atmosphere of dry nitrogen. The white crystalline material formed was separated from the mixture, washed with ethanol and dried under vacuum at a temperature of 0°C. 70 gram of product was obtained. The product compound had the empirical formula $AlPClH_{12}C_5O_9$.

Samples of the compound prepared above were dissolved in a number of solvents and each saturated solution was analysed. The results obtained are shown in Table I

TABLE I

Solvent	Solubility	Analysis				
	g solid/100ml solvent	Al	PO ₄	Cl	C ₂ H ₅ OH	Solvent
N-pentanol	10	0.86	3.04	1.13	5.90	89.07
Ethanol	11	0.96	3.39	1.26	94.39	—
Isopropanol	26	1.96	6.90	2.57	13.37	75.20
Methanol	90	4.19	14.75	5.50	28.60	49.66
Water	1000	7.15	25.19	9.40	48.88	9.38

Example 2

A clear solution was obtained by dissolving 26.7 gram of anhydrous aluminium chloride in 200 ml of methanol and adding 19.6 gram of 88% orthophosphoric acid. This solution was concentrated by evaporation to a thick syrup, useful as a coating solution hereinbefore described.

Example 3

A 10% by weight solution of the compound prepared as described in Example 1 in methanol was applied to a glass fibre immediately after it had been drawn. The coated glass fibre was then heated for 1 hour at 150°C. The tensile strength of the coated glass fibre was 50% higher on average than that of the un-

6 coated glass fibre drawn at the same time and under the same conditions.

Example 4

5 A solution containing 2% by weight of the compound prepared as described in Example 1 was made up in ethyl alcohol and to it was added 0.1% by weight of a wetting agent. Glass slides were then dipped into the solution, drained and heated at the following temperatures — 120°C, 250°C, 350°C, 450°C and 10 550°C for 2 hours. The slides were immersed in a suspension of cement in water. No reduction in the thickness of the film of aluminium phosphate on the glass occurred, as examined 15 microscopically and gravimetrically, after 65 hours of immersion at 20°C.

Example 5

400 gram of anhydrous aluminium chloride was dissolved in 300 ml of absolute ethanol

20 and the solution cooled in ice to a temperature of 0°C. 325 gram of 88% orthophosphoric acid was slowly added to the solution with stirring. 370 gram of a white crystalline solid with the empirical formula $\text{AlPClH}_{22}\text{C}_8\text{O}_8$ was filtered off and dried in a vacuum oven at 25 20°C for two hours.

10 gram of the solid was dissolved in 100 ml of ethanol. Carbon fibres were immersed in the solution, withdrawn and dried, first in air and then at 150°C for 15 minutes. The fibre, which 30 was found to have absorbed 5% of its weight after this treatment, was heated at 950°C for 5 hours in an atmosphere of dry nitrogen.

35 Similar weights of untreated carbon fibre and carbon fibre coated as above were treated for 2 hours in a stream of air. Table II shows the loss of weight of the carbon fibre samples when heated at four different temperatures and illustrates the protection against oxidative degradation afforded by the coating. 40

TABLE II

Loss of weight of coated and uncoated carbon fibre

Temperature °C	Uncoated fibre % weight loss in 2 hours	Coated fibre % weight loss in 2 hours
300	0	0
400	0	0
500	19	1.3
700	100	3.9

Example 6

45 Carbon fibre was degreased by immersion in trichloroethylene and passed through solutions of the compound prepared as described in Example 1 in three different solvents, water, ethyl

alcohol and methanol. The fibre was dried at 250°C and the coating cured by further heating at 500°C. The increased resistance to oxidation of the carbon fibre as a result of the coating is shown in Table III: 50

TABLE III

Coating Solution	Deposit % w/w*	% Loss in Weight after Heating in Air for 2 hours		
		500°C	600°C	700°C
2% complex in water	—	1.3	12.9	99.8
10% „ „ „	2	0.7	99.1	89.4
2% „ „ methanol	<0.1	1.3	27.5	96.9
10% „ „ „	2	0	18.5	97.3
2% „ „ ethanol	0.6	1.1	12.5	98.8
8.7% „ „ „	4.7	1.1	21.7	97.6
Double coating with 2% solution complex in ethanol	4.4	0	14.1	91.6
Untreated Fibre	—	56.4	100	100

* after drying at 250°C

Example 7

Carbon fibre was coated with 4% by weight of aluminium phosphate by treatment as in Example 6 with a 2% by weight solution of complex phosphate in ethyl alcohol. The weight loss of the coated fibre compared with

that of an uncoated fibre when they were both heated at 600°C in air was recorded at intervals of time. The results obtained are shown in Table IV, showing that the rate of oxidation is very considerably reduced by the presence of the coating.

TABLE IV

Time at 600°C in air (minutes)	Weight loss % w/w	
	uncoated fibre	coated fibre
15	60.6	5.4
30	97.1	7.9
45	98.5	9.0
60	99.6	10.1
75	100	10.1

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Example 8

The mechanical properties of uncoated carbon fibre and fibre coated as described in Example 7 were compared by measuring their Young's modulus and tensile strength. The

results shown in Table V were obtained, showing the beneficial effect of the coating on the mechanical properties after exposure of the fibre to oxidising conditions.

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TABLE V

Fibre and treatment	Modulus lb/in ²	Tensile Strength lb/in ²
(1) Uncoated Fibre	25—28 × 10 ⁶	28—29 × 10 ⁴
(2) Uncoated Fibre heated in air 10 minutes at 600°C	— too fragile to test —	—
(3) AlPO ₄ coated (4%)	22—25 × 10 ⁶	21—35 × 10 ⁴
(4) As (3) but heated in air 10 minutes at 600°C	29 × 10 ⁶	20 × 10 ⁴
(5) AlPO ₄ coated (3.6%)	23—33 × 10 ⁶	18—34 × 10 ⁴
(6) As (5) but heated in air 10 minutes at 600°C	21—23 × 10 ⁶	12—14 × 10 ⁴

Example 9

Carbon fibre was passed through molten aluminium. Only a few isolated globules of aluminium adhered to the fibre. Carbon fibre coated with 2% of aluminium phosphate by the process described in Example 7 was similarly passed through molten aluminium. It emerged with a continuous and adherent film of aluminium metal on its surface.

WHAT WE CLAIM IS:—

1. A method of coating a surface with aluminium phosphate of a deposit containing aluminium phosphate which comprises the steps of applying to the said surface a composition comprising a solution containing a halogen-containing complex phosphate of aluminium containing at least one chemically-bound molecule of a hydroxy compound R—OH wherein R is a hydrogen atom or an organic group, and removing the solvent of said composition.
2. A method as claimed in claim 1 wherein the complex phosphate contains at least one chemically-bound molecule of a hydroxy compound R—OH wherein R is a substituted or unsubstituted aliphatic hydrocarbon group.
3. A method as claimed in claim 1 or claim 2 wherein the complex phosphate contains at least one chemically-bound molecule of an aliphatic alcohol containing 1 to 4 carbon atoms.
4. A method as claimed in claim 3 wherein the hydroxy compound is ethyl alcohol.
5. A method as claimed in any one of the preceding claims wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus in the complex phosphate is substantially 1:1.
6. A method as claimed in any one of the preceding claims wherein the complex phosphate contains from 1 to 5 molecules of a hydroxy compound.

7. A method as claimed in any one of the preceding claims wherein the complex phosphate contains chemically-bound water and a chemically-bound organic hydroxy compound.

8. A method as claimed in claim 1 wherein the complex phosphate has the empirical formula $\text{AlPClH}_{2.5}\text{C}_6\text{O}_6$, $\text{AlPBrH}_{2.5}\text{C}_6\text{O}_6$, and $\text{AlPClH}_{11}\text{O}_8$.

9. A method as claimed in any one of the preceding claims wherein the composition additionally comprises an organic polymer.

10. A method as claimed in any one of the preceding claims wherein the solvent of the solution is water or an aliphatic alcohol containing 1 to 5 carbon atoms.

11. A method as claimed in any one of the preceding claims wherein the coating is heated to a temperature of at least 80°C.

12. A method as claimed in claim 11 wherein the coating is heated to a temperature in the range 100°C to 200°C.

13. A method as claimed in claim 11 or claim 12 wherein the duration of heating is at least 10 minutes.

14. A method as claimed in any one of the preceding claims wherein the composition additionally comprises a wetting agent.

15. A method as claimed in any one of the preceding claims wherein the surface coated is glass.

16. A method as claimed in claim 15 wherein the glass is in the form of glass fibre.

17. A method as claimed in claim 15 or claim 16 wherein the composition is applied immediately the glass is formed from its melt.

18. A method of coating glass substantially as described in either one of Examples 3 and 4.

19. Glass fibre coated with aluminium phosphate or a deposit containing aluminium phosphate.

20. Glass fibre coated with aluminium phosphate or a deposit containing aluminium phosphate by a method as claimed in any one of claims 1 to 18.
- 5 21. A method as claimed in any one of claims 1 to 14 wherein the surface coated is carbon.
22. A method as claimed in claim 21 wherein the carbon is in the form of carbon fibre.
- 10 23. A method as claimed in claim 21 or 22 wherein the coating is heated in an inert gas.
24. A method as claimed in any one of claims 21 to 23 wherein the coating is heated at a temperature in the range 100°C to 500°C.
- 15 25. A method of coating carbon substantially as described in any one of Examples 5 to 7.
26. Carbon fibre coated with aluminium phosphate or a deposit containing aluminium phosphate.
- 20 27. Carbon fibre coated with aluminium phosphate or a deposit containing aluminium phosphate by a method as claimed in any one of claims 21 to 25.
- 25 28. Carbon fibre as claimed in claim 26 or claim 27 when surface-coated with aluminium metal.
29. A method as claimed in any one of claims 1 to 14 where the surface coated is a ceramic material.
30. A method as claimed in any one of claims 1 to 14 where the surface coated is a metal. 30
31. A method as claimed in any one of claims 1 to 14 where the surface coated is an organic polymer. 35
32. A body having a surface coated by a method as claimed in any one of claims 1 to 18, 21 to 25 and 29 to 31.
33. A coating composition comprising a solution containing a halogen-containing complex phosphate of aluminium containing at least one chemically-bound molecule of a hydroxy compound R—OH which is an aliphatic alcohol containing 1 to 4 carbon atoms. 40
34. A coating composition according to claim 33, substantially as described in any of the examples. 45

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